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(54) Forming metal film patterns on substrates

(57) A method of forming a metal film pattern on a substrate, comprising forming a positive or negative image of the pattern, applying that image to the substrate by depositing a material thereon, coating the substrate with a metal or metal alloy film e.g of :- gold, copper, silver, aluminium, brass or beryllium copper), in an ion deposition process and applying a solvent to the metal coated substrate so as to selectively remove metal from regions thereof to leave the desired metal film pattern on the substrate. The image is applied to the substrate in a dry toner photocopier and formed thereon in a fused ferrite filled styrene acrylic copolymer plastics material. The pattern of metal tracks may be formed on more than one surface of said substrate. The image may be either a positive or negative image of the pattern and the solvent be selected to remove the metal film adhering to the substrate (e.g. methyl alcohol) or to the fused toner image (e.g. acetone, methyl ethyl ketone, xylene or toluene). The substrate may be porous or non-porous.

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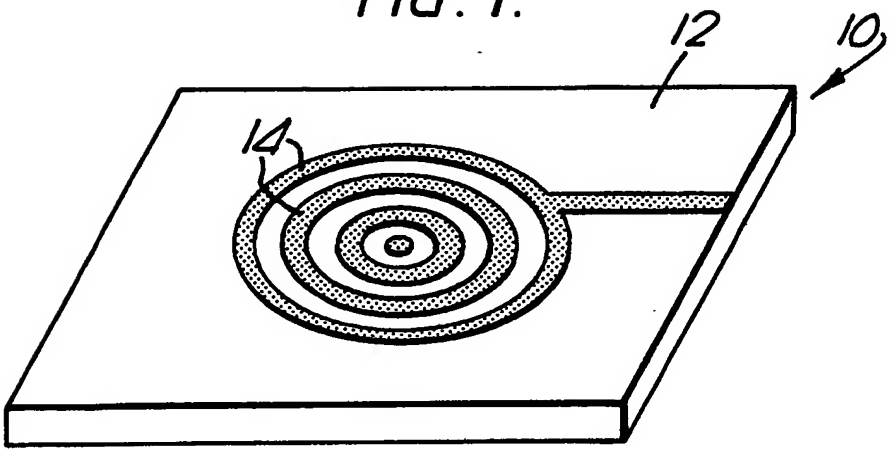
FIG. 1.



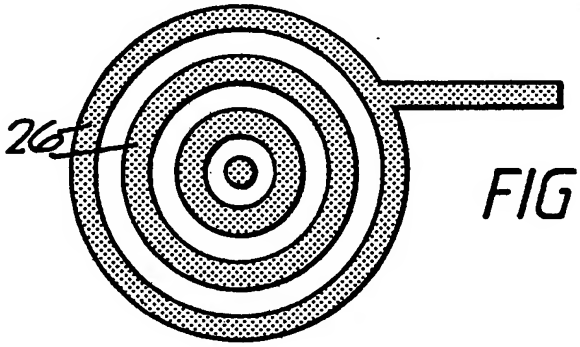


FIG. 3A

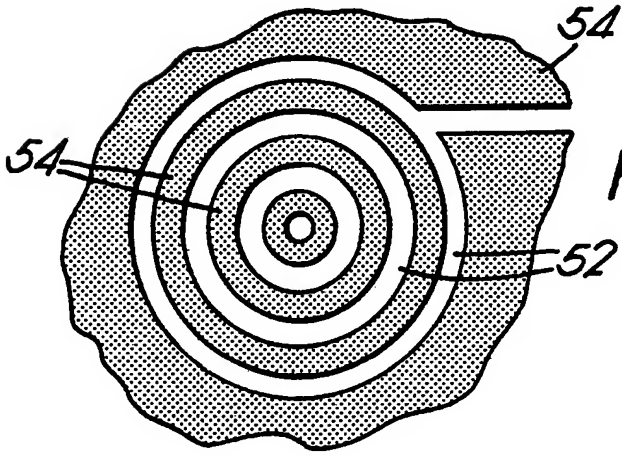


FIG. 3B

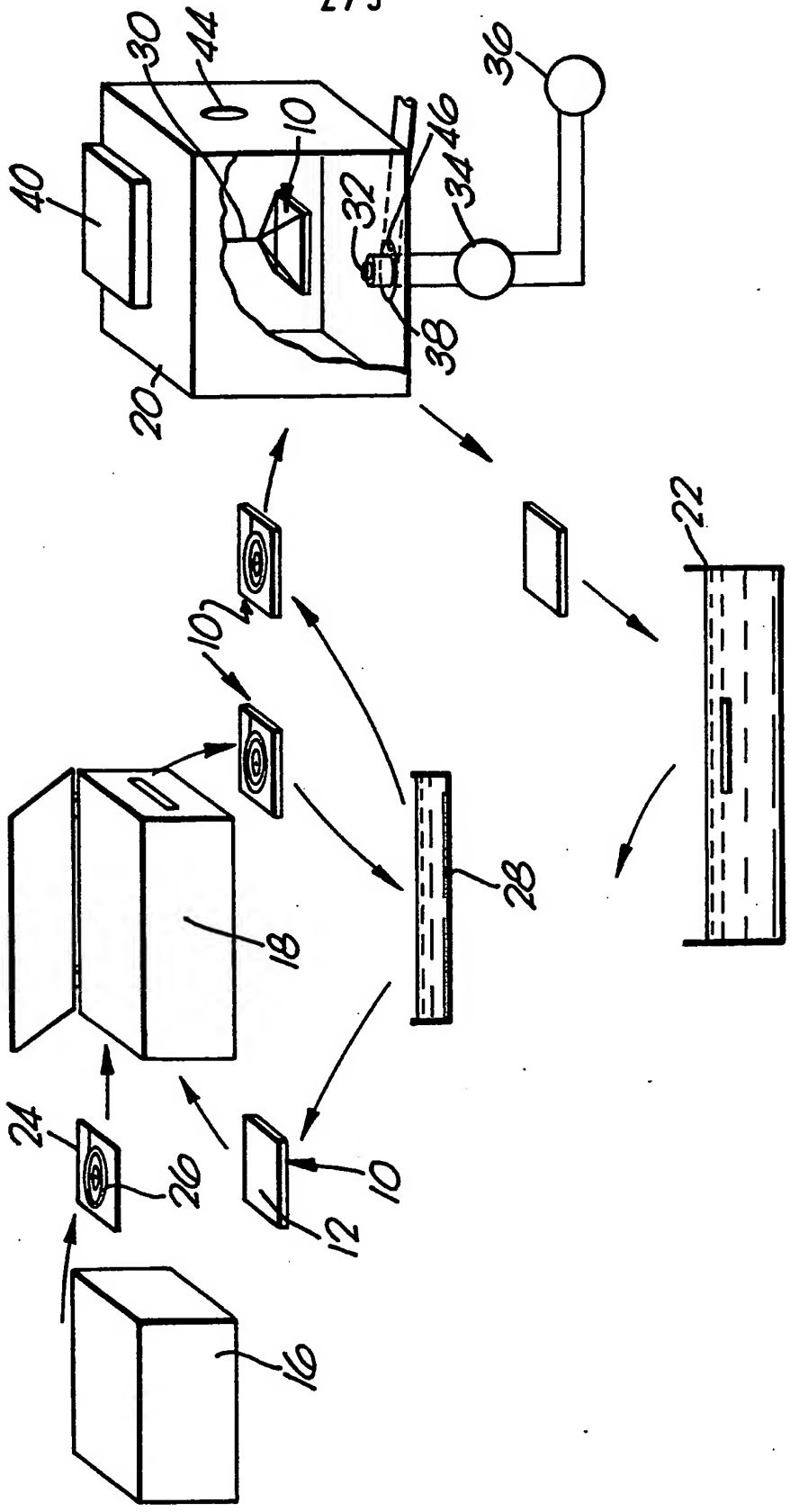


FIG. 2

FIG. 4A

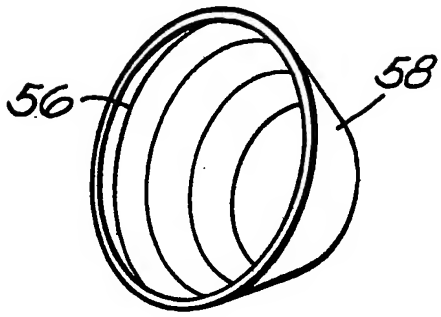
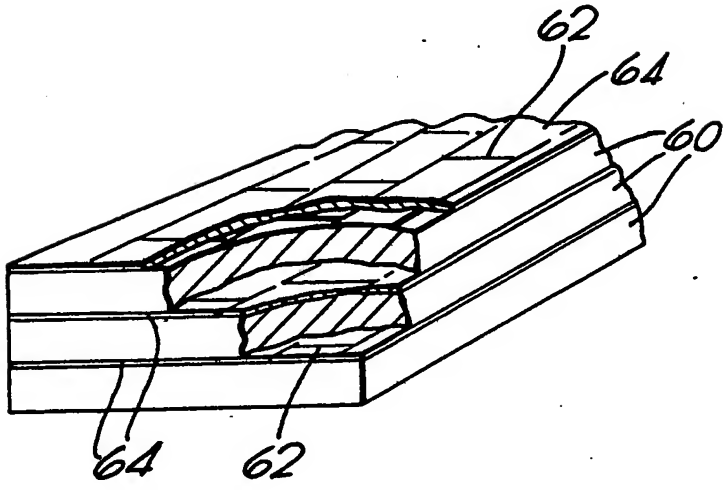


FIG. 4B



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METAL FILM PATTERNS ON SUBSTRATES

DESCRIPTION

The invention concerns the production of metal film patterns on substrates in particular the production of substrates having a desired metal film pattern on at least one surface thereof.

In this specification and in the claims annexed hereto the term substrate encompasses any article having a surface upon which it is desired to provide a metal film pattern. The articles will often be in the form of flat sheets or lamella, but may also comprise articles of other, non-flat shapes and complex, e.g. laminated, structures having metal film patterns formed on one or both major surfaces thereof as well as within the article.

Usually the production of a pattern (which may be complex in design) of metal film tracks on a substrate - for example, in the formation of printed circuit boards or of antenna - requires the pattern be prepared by a photo-chemical etching process.

Such processes are expensive as they require the formation of a high quality photographic image of the pattern to be reproduced on the substrate and the production of a photographic negative of that image which may be projected onto the substrate. In general terms these processes are of commercial use only when it is desired to produce a large number of substrates each carrying the same metal film pattern as when it is desired to form only one or two items, the unit cost of preparing the negative is too high in terms of both direct and indirect costs.

We now disclose a novel process enabling such articles to be made more readily and at less cost than has until now been possible and which, moreover, may be used to produce a limited number of the finished articles without

incurring economic penalties.

In one aspect the invention provides a method of forming a desired metal film pattern on a substrate which comprises the steps of:- forming an image correlated to the desired pattern, applying that image to the substrate by depositing a material thereon in accordance with said image, depositing a metal film onto the substrate by metal ion deposition, and applying a solvent to the metal coated substrate so as to selectively remove metal from regions thereof corresponding to the said image so as to leave the desired metal film pattern on the substrate.

Desirably said image is applied to the substrate in an electrostatic image transfer process such as a dry toner photocopier.

Preferably the image is formed on the substrate in a fused styrene acrylic copolymer plastics material filled with iron oxide - ferrite.

Any suitable metal or metal alloy may be ion deposited onto the substrate and is preferably one of:- gold, copper, silver, aluminium, brass or beryllium copper.

A desired metal film pattern may be formed on more than one surface of said substrate.

The substrate may be coated with an electrically non-conductive lacquer after formation of the desired pattern or patterns thereon.

A plurality of substrates may be conjoined after the formation of desired patterns thereon.

The image may be a positive image of the desired pattern and the solvent be used to selectively remove metal adhering directly to the substrate without interposition of said fused toner. In this case the solvent used is methyl alcohol.

Alternatively, said image may be a negative image of the desired pattern and the solvent be used to selectively remove metal adhering to said fused toner forming said image on the substrate. In this case the

solvent preferably comprises one or more of acetone, methyl ethyl ketone, xylene and toluene.

The substrate may be non-porous and the thickness of the metal film ion deposited thereon desirably will not exceed one micron.

The substrate may be of a plastics material such as acetate, or of a thermoplastics material such as polyethersulphone, polyetherimide, and polyetheretherketone, formed by moulding, rolling or pressing, with or without the inclusion of glass or other fibres reinforcement.

Alternatively the substrate may be of a porous material such as paper, board, card, woven or laid natural or synthetic materials. The substrate may for example be formed by weaving or laying up a thermoplastics material such as polyethersulphone, polyetherimide, and polyetheretherketone.

A process for the manufacture of a substrate embodying the invention will now be described with reference to the accompanying drawings, in which:-

Figure 1 illustrates a substrate having a desired metal film pattern formed thereon in accordance with processes embodying the invention,

Figure 2 schematically illustrates equipment in which the processes are carried out,

Figure 3 illustrates at A and B respectively images used in different processes embodying the invention to produce the substrate shown in Figure 1, and

Figure 4 illustrates various articles made in accordance with the invention.

Figure 1 illustrates a substrate 10 in the form of a flat sheet of material on one surface 12 of which has been formed a number of concentric metal tracks 14 (e.g. of gold) enabling the substrate to function as an antenna.

This pattern of metal tracks 14 on substrate 10 is formed by first forming a master of an image correlated to the desired pattern of those tracks - for example by making

use of a digital plotter (such as shown at 16 in Figure 2), in a computed aided design - CAD - process). The correlation between this image and the desired pattern 14 may be that the image is a positive image of the desired pattern (as shown in Figure 3A), or a negative (reverse) image of the desired pattern (such as shown in Figure 3B).

The image is then applied to surface 12 of substrate 10 by depositing a material on that surface in accordance with the image - for example by copying the master image onto surface 12 of substrate 10 in a dry toner photo-copying machine 18 so that the image is reproduced on surface 12 of substrate 10 in the fused toner used in the photocopier.

Thereafter the whole of surface 12 of substrate 10 is coated with a film of the selected metal or metal alloy - for example in a vacuum metal-ion deposition chamber 20 - to a desired depth and after formation of the metal coating thereon the substrate has a suitable solvent applied to it - for example in a bath as shown at 22 in Figure 2 - so as to selectively remove metal corresponding to the image - that is to say either from the regions of the substrate upon which the image was formed (if the image was a negative or reverse image of the desired pattern) or from the regions of the surface 12 upon which the image was not formed (if the image was a positive or direct image of the desired pattern). Thus the desired pattern 14 of metal film tracks is left on surface 12 of substrate 10.

A first example of the invention forms in fused toner a positive image of the desired pattern 14 of metal tracks on substrate 10 - to form the pattern shown in Figure 1 the image would be as shown in figure 2A - and the substrate is non-porous, e.g. it is an acetate sheet.

The image is first drawn, sketched or otherwise produced (desirably with a digital plotter in a CAD design process) at 16 possibly to a scale significantly larger or smaller than that at which the final pattern is to be

produced on a paper sheet 24. In this embodiment the dark areas 26 of the image on sheet 24 correspond to the metal tracks desired to form the pattern 14 on the finished substrate 10.

Sheet 24 is taken to photocopier 18 and the image on it photocopied onto the substrate 10 which, as noted, comprises an acetate sheet.

Before passing the acetate sheet to the photocopier the sheet is thoroughly cleaned as indicated at 28 by washing in warm soapy water, rinsing in de-ionised water and then drying in warm air to remove any surface contaminents.

The toner used in the photocopier is preferably a styrene acrylic copolymer material filled with iron oxide - ferrite, and a duplicate of the image on paper sheet 24 is formed on surface 12 of substrate 10 as a fused film of this toner powder.

It is possible by using the reduction and/or enlargement facilities of modern photocopiers to produce the desired image on the acetate sheet at a different scale to that at which the image was drawn on sheet 24 if desired.

The acetate sheet is removed from photocopier 18 and after it is again thoroughly cleaned - washed, rinsed and dried in the same manner once again - is hung on a rotatable support 30 in vacuum chamber 20. The metal to form the ion deposited pattern of tracks on the acetate sheet is the target of a DC Magnetron 32 (for example a Research "S" gun made by Sputtered Films Inc.).

By use of a diffusion pump 34 and rotary pump 36 chamber 20 is evacuated. A baffle valve 38 is provided between chamber 20 and diffusion pump 34 which may be partially closed to throttle the effect of the pump and allow selected high purity gases to be introduced into the vacuum chamber at a controlled low pressure. A 13.65MHz Radio Frequency (RF) supply is fed at 40 to the top of chamber 20 and the acetate sheet 10 within the chamber is

connected to this supply by support 30.

The chamber preferably has a port 44 through which its operation may be viewed.

The pressure in chamber 20 is reduced by operation of pumps 34 and 36 to lower than 9×10^{-6} Torr (preferably to approximately 5×10^{-6} Torr to ensure the system is clean. The baffle valve 38 is operated and Argon bled into the chamber from inlet 46 at 8mTorr and an RF signal applied to the acetate sheet at approximately 50 Volts.

After approximately one minute, when the system has stabilised, 150 Watts of DC power is applied to the gun 32 and the acetate sheet within the chamber is rotated at approximately 10 revolutions per minute.

Once the gun 32 has stabilised (after approximately two minutes) the pressure in chamber 20 is further reduced to 3.5mTorr, the power to the RF supply is reduced to a minimum and the power to the gun 32 is gradually increased.

Over a period of three minutes the power to gun 32 is increased to a maximum of 1 KW and the RF power to the acetate sheet is reduced to zero. The acetate sheet is then left in chamber 20 and coated with metal by operation of the gun 32 for sufficient time - between five and 60 minutes - to produce the desired metal layer thickness (0.5 to 1 micron) on sheet 10.

Once the desired thickness has been obtained the DC power and gas supplies are turned off, air is admitted to chamber 20 and the acetate sheet 10 removed from it.

The noted conditions in the chamber 20 provide a uniform metal coating on the acetate sheet 10 over the whole of its surface i.e. both the parts carrying the fused toner image and the parts which do not carry that image.

As will be appreciated the by those skilled in the art of metal ion deposition techniques, the thickness of the metal film layer deposited onto the substrate is proportional to the power applied to the gun, the metal

being deposited and the time for which the substrate is treated. In general to produce a layer of given thickness in pure metal higher power must be applied to the gun, and/or the the substrate must be treated for a longer period than if a metal alloy film was being deposited on the substrate.

After removal from chamber 20 the acetate sheet 10 is immersed in a bath of industrial grade methyl alcohol as indicated at 22 for no more than five minutes. After removal from the bath of methyl alcohol the sheet is hand scrubbed with a rough cloth soaked in methyl alcohol, this acts to lift from the surface of the sheet the metal layer ion deposited directly onto the acetate but not to remove the metal layer ion deposited onto those areas of the sheet which carries the fused toner image. During this scrubbing process the sheet is washed repeatedly with methyl alcohol to ensure metal lifted from the sheet is carried away.

Treatment in this way lifts the metal layer ion deposited onto those areas of the sheet which do not carry the fused toner image so leaving on sheet 10 the metal layer deposited onto that image.

This is achieved because of the way in which the metal is deposited onto the substrate in the vacuum ion deposition chamber - the metal at least initially being deposited in the form of crystals aligned normally of the surface of the substrate such that the metal film is microporous enabling the solvent used to pass between the crystals and reach the surface thereunder.

The solvent used - methyl alcohol - dissolves the bond between the upper surface of the acetate sheet and the metal deposited thereon (allowing the metal deposited thereon to be removed) without deleteriously affecting the substrate material and without affecting the bonding between the fused toner and the substrate. Whilst not wishing to be bound by the following explaination, it is believed that the solvent selectively lifts the metal on acetate surface but

not on the fused toner image because the bonding between the metal film and the acetate substrate involves an aqueous interlayer which enables the solvent readily to detach the metal from the substrate. This aqueous interlayer does not appear between the fused toner and the metal ion deposited thereon.

To enhance this effect is is desirable that the metal film ion deposited onto the substrate be no more than a predetermined thickness (e.g. one micron) which is, as noted above, a function of the characteristics of the ion deposition process which has been used.

If desired the thickness of the metal pattern may be increased by returning the substrate to the ion deposition chamber 20 after treatment with the solvent so as to deposit further metal (the same or a different metal) thereon to increase the thickness of the metal film overlying the fused toner image and thereafter using the same or another solvent to remove the unwanted metal.

If desired the substrate may be provided on both surfaces with the same or a different pattern of metal tracks. This may be achieved either by following the process outlined to provide a desired pattern on one surface of the substrate above and then passing the substrate through the process for a second time to form a second desired pattern on the other surface of the substrate, or by forming the same or different desired patterns onto both surfaces of the substrate before it is passed to the vacuum chamber 20 and then ion-depositing a metal layer onto both surfaces of the substrate. To enhance this second method the substrate may be arranged for rotation about two orthogonal axes whilst in the vacuum chamber so that both surfaces of the substrate are presented to the gun 32.

An advantage of this modification to the process is the more rapid production of a substrate having complex pattern metal films on both sides thereof - e.g. in the production of printed circuit boards.

A second example of putting the invention into effect to be described provides that the master image is a negative or reverse image of the desired pattern 14 of tracks - to be formed on the substrate such as is shown in Figure 2B where the desired pattern of tracks corresponds to the light areas 52 between the circular dark bands 54 and that the substrate is of a porous material - e.g. plain paper.

The master image is prepared on sheet 24 in the same way as in the first example given save that the image produced is, as noted, the reverse of the desired final pattern 14.

The paper sheet to form the substrate is thoroughly cleaned (in a manner which will not effect the structure of the sheet) to remove any surface contaminents.

Again the toner used in photocopier 18 is a styrene acrylic copolymer material filled with iron oxide - ferrite.

Both the master copy 24 and the sheet 10 upon which the desired pattern 14 is to be produced are taken to photocopier 18 and the image on sheet 24 is reproduced on one surface 12 of sheet 10 as a fused film of the toner.

After the sheet 10 has had the image formed thereon in fused toner powder it is cleaned of contaminents it may have picked up and then has ion deposited upon it a layer of metal in the manner already described in the first example above.

After removal from the ion deposition chamber 20 the paper sheet 10 is immersed in a bath of industrial acetone or other suitable solvent (e.g. methyl ethyl ketone, xylene or toluene) for sufficient time for the solvent to fully penetrate the porous substrate (e.g. for approximately five minutes) and dissolve the plastics/polymer binder of the fused toner reverse image. After removal from the solvent bath sheet 10 is hand rubbed with cotton wool soaked in solvent and this acts to lift from the surface of the

sheet the metal layer ion deposited onto the fused toner covered areas but not to remove the metal layer ion deposited directly onto the paper.

Treatment in this way lifts the metal layer ion deposited onto those areas of the sheet which carry the fused toner image so leaving on the sheet the metal layer deposited onto remainder of the sheet, which, as the fused toner image was the reverse of the desired pattern has the result that the desired pattern of metal tracks is left on the surface of the sheet.

This is achieved principally because of the porous nature of the substrate which allows the solvent to pass through it - without affecting the material of the substrate - and attack the toner fused onto the substrate surface. As the toner is lifted from the substrate it takes with it the metal ion deposited onto it leaving the desired pattern of tracks on the substrate surface.

It will be appreciated that with this second example there is no limitation on the thickness of the metal layer which may be deposited onto the substrate - whatever the thickness of the metal layer deposited onto the substrate that above the fused toner will be lifted off when the toner is removed from the substrate.

If desired the substrate may be provided on both surfaces with the same or a different pattern of metal tracks. This may be achieved by following the process outlined to provide a desired pattern on one surface of the substrate above and then passing the substrate through the process for a second time to form a second desired pattern on the other surface of the substrate. The process may be enhanced by forming in fused toner negatives of the same (or different) desired patterns on both surfaces of the substrate before it is passed to the vacuum chamber 20 for the first time.

It will be seen that any porous substrate may be used - in addition to the paper described substrates of

board or card, or of cloth made by laying up or weaving a natural or synthetic material such as a thermoplastics material selected from the group comprising:- polyethersulphone, polyetherimide, and polyetheretherketone may be used.

The use of the particularly described solvents to remove the fused toner image from paper substrate is not limitative and other solvents may be used which are not inimicable to the material of the substrate.

It will further be seen that the examples described are not limitative and that a positive image of the desired pattern may be used with a non-porous substrate and a negative image with a porous substrate if desired by selection of the material of the substrate and of the solvent used.

As described the pattern is formed on a flexible substrate however, it will be appreciated that rigid or semi-rigid substrates may be used.

The selection of the metal forming the coating on the substrate is determined by the particular application in which the substrate is to be used.

It will be appreciated that once the desired pattern has been formed on the substrate (on one or both of its surfaces) the substrate may be folded, bent or otherwise shaped if desired to accomodate different uses - for example a dish antenna as shown at Figure 4A, in which a substrate 56 substantially the same as that described above has been attached to an appropriately shaped concave dish 58 to form the antenna.

To this end the pattern produced on the substrate in the process noted above may be modified in a CAD process to take account of the subsequent flexure of the substrate.

Again it will be appreciated that if the image is formed on a flexible sheet is is possible for that sheet to be bent or even pre-formed to a predetermined, desired shape prior to its placement in the vacuum chamber 20.

It will also be seen that the substrate produced by the method of the invention may be subsequently further processed to produce a desired product. The substrate may for example be coated with a layer of material to protect the metal pattern formed thereon, or even be used in a "stacking" process to provide a laminate the different lamella within which have the metal pattern tracks formed thereon as shown at Figure 4B. Figure 4B shows a number of substrates 60 each having a pattern of metal tracks 62 formed thereon by the methods discussed above which have thereafter been covered with layers 64 of electrically non-conductive lacquer and then formed (e.g. making use of a suitable adhesive) into a laminate structure having desired patterns of metal tracks formed on and within the article.

It will be appreciated that the same image correlated to the pattern to be reproduced on the substrate may be copied onto more than one substrate - indeed the image may be copied onto as many substrates (of the same or different material) as desired. It will also be seen that the image correlated to the desired pattern may readily and simply be altered if desired when it is thought necessary and/or desirable to alter the pattern to to be formed - e.g. as part of a development programme when a number of similar but different patterns may need to be tested.

It will be seen that the method of the invention overcomes the difficulties found in the known photo-chemical etching process, namely the high cost involved in producing the required high quality photographic image of the pattern to be reproduced and the production of a photographic negative of that image which may be projected onto the substrate.

Futhermore it will be seen that the method of the present invention enables relatively few substrates to be economically made having the same pattern - the desired pattern (or its reverse) being readily reproduced and photocopied onto the substrate to be formed.

CLAIMS

1. A method of forming a desired metal film pattern on a substrate which comprises the steps of:- forming an image correlated to the desired pattern, applying that image to the substrate by depositing a material thereon in accordance with said image, depositing a metal film onto the substrate by metal ion deposition, and applying a solvent to the metal coated substrate so as to selectively remove metal from regions thereof corresponding to the said image so as to leave the desired metal film pattern on the substrate.

2. A method as claimed in claim 1, wherein said image is applied to the substrate in an electrostatic image transfer process such as a dry toner photocopier.

3. A method as claimed in claim 2 wherein the image is formed on the substrate in a fused styrene acrylic copolymer plastics material filled with iron oxide - ferrite.

4. A method as claimed in any one of the preceding claims wherein the metal is one of:- gold, copper, silver, aluminium or a metal alloy such as brass or beryllium copper.

5. A method as claimed in any one of the preceding claims, wherein a desired metal film pattern is formed on more than one surface of said substrate.

6. A method as claimed in any one of the preceding claims wherein the substrate is coated with an electrically non-conductive lacquer after formation of the desired pattern or patterns thereon.

7. A method as claimed claims 6, wherein a plurality of substrates are conjoined after the formation of desired patterns thereon.

8. A method as claimed in any one of the preceding claims wherein said image is a positive image of the desired pattern and the solvent is used to selectively remove metal adhering directly to the substrate without interposition of said first material.

9. A method as claimed in claim 3 and claim 8 wherein the said solvent is methyl alcohol.

10. A method as claimed in any one of the preceding claims wherein said image is a negative image of the desired pattern and the solvent is used to selectively remove metal adhering to said first material forming said image on the substrate.

11. A method as claimed in claim 3 and claim 10 wherein said solvent comprises one or more of acetone, methyl ethyl ketone, xylene and toluene.

12. A method as claimed in claim 9 any one of the preceding claims the substrate is non-porous and the thickness of the metal film ion deposited thereon does not exceed one micron.

13. A method as claimed in claim 12 wherein the substrate is of a plastics material such as acetate, or of a thermoplastics material such as polyethersulphone, polyetherimide, and polyetheretherketone, formed by moulding, rolling or pressing.

14. A method as claimed in any one of claims 1 to 11, wherein the substrate is porous and is of paper, board, card, woven or laid natural or synthetic materials.

15. A method as claimed in claim 14 wherein the substrate formed by weaving or laying up a thermoplastics material such as polyethersulphone, polyetherimide, and polyetheretherketone.

16. A substrate having a desired metal film pattern thereon made in accordance with any one of the preceding claims.

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